

文章编号: 1006-9941(2007)05-0511-04

高氯酸·四氨·双(5-硝基四唑)合钴(III)(BNCP)的晶体结构

盛涤伦, 马凤娥, 张裕峰, 朱雅红, 陈利魁, 杨斌

(陕西应用物理化学研究所, 陕西 西安 710061)

摘要: 制备了高氯酸·四氨·双(5-硝基四唑)合钴(III)(BNCP)的单晶,用 X-ray 单晶面衍射仪对其晶体进行了结构测定。证实该晶体属单斜晶系,空间群为 $P2(1)/n$ 。晶胞参数为: $a = 10.0149(11) \text{ \AA}$; $b = 10.5387(11) \text{ \AA}$; $c = 14.8241(16) \text{ \AA}$ 。 $V = 1479.2(3) \text{ \AA}^3$, $Z = 4$, $D_c = 2.050 \text{ mg} \cdot \text{mm}^{-3}$, $\mu = 1.421 \text{ mm}^{-1}$, $F(000) = 928$,并得到了 BNCP 的原子坐标、等效温度因子、键长、键角和扭转角等数据。根据测试参数,分析了 BNCP 的结构特点和分解机理。

关键词: 物理化学; 起爆药; 高氯酸·四氨·双(5-硝基四唑)合钴(III)(BNCP); 晶体结构; 单斜晶系

中图分类号: O64; TJ55

文献标识码: A

1 引言

高氯酸·四氨·双(5-硝基四唑)合钴(III)(BNCP)自 1986 年首次被合成以来^[1],现已作为一种性能优异的新型起爆药得到广泛研究和应用^[2-7],它具有安全性好,耐热性好,起爆性能好,可以实现 BNCP 雷管的单一装药,能够部分代替 $\text{Pb}(\text{N}_3)_2$ 、斯蒂芬酸铅和 CP 用于火焰雷管、桥丝式雷管、DDT 雷管、SCB 雷管及激光起爆和点火元件中。

为了更好地表征 BNCP 的结构,为今后进一步理论研究提供基础数据,本课题组制备了 BNCP 单晶,测定了它的晶体结构。结果表明:样品的晶系、空间群和晶胞参数与 B. Morosin 等人^[8]报道的数据基本吻合。说明我们制备的 BNCP 与美国 Sindhia 国家实验室产品的晶体结构完全相同,也是顺式结构,不存在异构体。但该文主要是对比 293 K 和 213 K 下 BNCP 晶体结构的区别,仅仅给出了 BNCP 的基本晶胞参数,没有给出 BNCP 的原子坐标、等效温度因子、键长、键角和扭转角等详细晶体学结构数据,也没有对 BNCP 晶体特征进行分析。本文首次报道了这些数据,并依据数据进行了晶体结构特征和分解机理的解析,这对于将来解释化合物的感度机理、量子化学计算以及制作三维分子模型都是非常重要的。

2 BNCP 单晶的制备

在烧杯中依次加入一定量的蒸馏水、高氯酸和

BNCP 合成品。匀速搅拌下缓慢用油浴加热,使 BNCP 完全溶解。然后加入少量的高氯酸铵溶液。过滤此母液,将滤液冷却至室温。放置若干天后得到橘黄色大结晶 BNCP。从中挑选出适当大小的单个结晶颗粒进行 X-ray 单晶分析。

样品质量分析结果为(%):实测值(计算值): Co^{3+} 13.82(12.97), NH_3 14.77(14.99), ClO_4^- 21.88(21.87)(其中样品含水为 0.01%)。样品的红外分析、DSC 热分析图谱与百克量合成产品相同。因而获得的大结晶 BNCP 的质量符合合成批技术要求。

3 BNCP 晶体结构测定

选取尺寸为 $0.45 \text{ mm} \times 0.42 \text{ mm} \times 0.30 \text{ mm}$ 的 BNCP 单晶,在德国 Bruker smart apex II CCD 型 X-ray 单晶面探仪上,用 MoK_α 射线($\lambda = 0.71073 \text{ \AA}$)扫描。衍射实验温度:298(2) K,数据收集的 θ 角范围: $2.17^\circ \sim 25.10^\circ$,衍射指标: $-10 \leq h \leq 11$, $-6 \leq k \leq 12$, $-17 \leq l \leq 17$ 。共收集衍射点 7243 个,其中独立衍射点 2623 个 [$R(\text{int}) = 0.0315$]。 $\theta = 25.10^\circ$ 的完整度为 99.5%。最大与最小透过率为:0.6752 和 0.5673。精修方法:基于 F^2 的全矩阵最小二乘法。数据/限制/参数的个数:2623/0/240。基于 F_2 的拟合优度:1.048。对于 $I > 2\sigma(I)$ 数据的最终残差因子 $R_1 = 0.0418$, $wR_2 = 0.1220$;对所有数据的残差因子 $R_1 = 0.0440$, $wR_2 = 0.1235$ 。消光系数为:0.0008(8)。最大衍射峰和孔:1.237 和 $-0.673 \text{ e} \cdot \text{\AA}^{-3}$ 。

4 BNCP 的晶体结构描述

经过德国 Bruker AXS 的 SHELXTL 程序计算,BNCP 晶体属于单斜晶系,空间群为: $P2(1)/n$ 。晶胞参数

收稿日期: 2006-11-06; 修回日期: 2007-01-03

作者简介: 盛涤伦(1956-),男,研究员级高工,硕士研究生,主要从事新型火工药剂的研究与应用开发工作。e-mail: shdl1998@sina.com

为 $a = 10.0149(11) \text{ \AA}$, $\alpha = 90^\circ$; $b = 10.5387(11) \text{ \AA}$, $\beta = 109.0140(10) \text{ \AA}$, $c = 14.8241(16) \text{ \AA}$, $\gamma = 90^\circ$. $V = 1479.2(3) \text{ \AA}^3$, $Z = 4$, $D_c = 2.050 \text{ Mg} \cdot \text{mm}^{-3}$. $\mu = 1.421 \text{ mm}^{-1}$, $F(000) = 928$.

BNCP 分子结构如图 1 所示。原子坐标和等效温度因子、键长与键角、扭转角数据分别列于表 1 ~ 表 4。

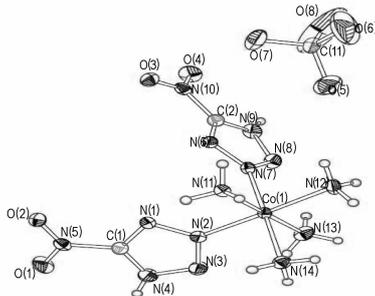
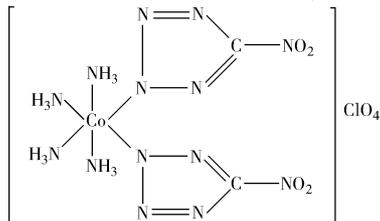


图 1 BNCP 晶体的分子结构

Fig. 1 Molecular structure of BNCP

5 分析与讨论

分析表明: BNCP 的化学结构为



(1) 两个大配位体 5-硝基四唑是相邻结构,并非上下对称结构,并且是由五员环上 2 位氮原子的孤对电子与中心 Co 原子配位。由于大配位体的占位效应,使得 Co 原子所连接的 6 个氮原子所形成的键角不是严格的 90° 或 180° ,而是各有偏差,最大达到 2° 左右。

(2) 由于硝基的强吸电子效应和 N2、N7 的供电子效应,使五员环母体不能保持正五边形的几何构型,其五边形平面结构发生了变形, C1、N2 和 C2、N7 为顶点的键角都较大,并且环的平面分别扭曲 0.4° 和 0.8° ,两环的平面存在非 90° 的夹角。

(3) 五员环上 C—N 和 N—N 键长的实测值(例如: N(1)—C(1): 1.312 \AA , N(1)—N(2): 1.329 \AA) 都分别略小于 C=N 和 N=N 双键的标准平均键长值 (C=N: 1.35 \AA , N=N: 1.25 \AA),说明五员环形成了双键共轭体系。硝基与五员环相连的 C—N 键实测值为: N(5)—C(1): 1.446 \AA , N(10)—C(2): 1.439 \AA ,接近 C—N 单键的标准平均键长 1.48 \AA ,表明硝基与五员环具有单键连接特性 (C=N 双键的标准平均键长为: 1.35 \AA),未能形成共轭体系。

(4) 钴原子与氨、5-硝基四唑的 6 个氮原子连接的键长均较长,达到 $1.923 \sim 1.957 \text{ \AA}$,预示键合较弱。因此, BNCP 的分解反应极有可能是先解离放出氨、四唑,然后再与高氯酸根进行小分子的氧化还原反应。

表 1 BNCP 的各原子坐标和等效温度因子

Table 1 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for BNCP

atom	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	$U(\text{eq}) \times 10^3 / \text{\AA}^2$
Co(1)	3242(1)	2222(1)	598(1)	21(1)
N(1)	3268(3)	-519(3)	671(2)	26(1)
N(2)	2676(3)	546(3)	836(2)	26(1)
N(3)	1639(4)	314(3)	1181(3)	43(1)
N(4)	1542(4)	-937(3)	1260(3)	45(1)
N(5)	2824(3)	-2720(3)	918(2)	34(1)
N(6)	6091(3)	1185(3)	1309(2)	25(1)
N(7)	5117(3)	1914(3)	1478(2)	24(1)
N(8)	5581(4)	2408(3)	2350(2)	37(1)
N(9)	6891(3)	2001(3)	2761(2)	39(1)
N(10)	8462(3)	613(3)	2270(2)	36(1)
N(11)	3812(3)	1560(3)	-443(2)	23(1)
N(12)	3861(4)	3902(3)	339(2)	37(1)
N(13)	2674(4)	2899(3)	1648(2)	42(1)
N(14)	1327(3)	2508(3)	-268(2)	32(1)
C(1)	2530(3)	-1380(3)	941(2)	27(1)
C(2)	7151(4)	1278(3)	2115(2)	27(1)
O(1)	2238(4)	-3441(3)	1306(3)	57(1)
O(2)	3655(3)	-3038(3)	510(2)	41(1)
O(3)	8605(3)	1(3)	1615(2)	45(1)
O(4)	9343(3)	712(3)	3061(2)	59(1)
Cl(1)	9142(1)	3944(1)	1460(1)	42(1)
O(5)	7695(5)	4142(5)	1379(4)	93(1)
O(6)	9258(10)	4798(6)	776(6)	167(3)
O(7)	9337(4)	2740(3)	1089(3)	72(1)
O(8)	10035(10)	4201(11)	2273(5)	281(8)

Note: $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

表 2 BNCP 的氢原子坐标和等效温度因子

Table 2 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for BNCP

hydrogen	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	$U(\text{eq}) \times 10^3 / \text{\AA}^2$
H(4)	969	-1357	1470	54
H(9)	7448	2172	3326	47
H(11A)	4740	1658	-307	35
H(11B)	3362	1978	-977	35
H(11C)	3597	739	-523	35
H(12A)	4601	3822	136	56
H(12B)	4104	4364	871	56
H(12C)	3160	4285	-108	56
H(13A)	2049	2378	1763	62
H(13B)	2286	3661	1489	62
H(13C)	3429	2964	2169	62
H(14A)	1097	1896	-706	48
H(14B)	1285	3256	-554	48
H(14C)	725	2500	61	48

表3 BNCP分子的键长与键角

Table 3 Bond lengths [Å] and angles [deg] for BNCP

bond	bond lengths / Å	bond	bond lengths / Å	bond	bond lengths / Å	bond	bond lengths / Å
Co(1)—N(2)	1.923(3)	N(4)—C(1)	1.312(5)	N(9)—H(9)	0.8600	N(13)—H(13A)	0.8900
Co(1)—N(7)	1.933(3)	N(4)—H(4)	0.8600	N(10)—O(3)	1.213(4)	N(13)—H(13B)	0.8900
Co(1)—N(11)	1.942(3)	N(5)—O(1)	1.214(4)	N(10)—O(4)	1.221(4)	N(13)—H(13C)	0.8900
Co(1)—N(14)	1.953(3)	N(5)—O(2)	1.224(4)	N(10)—C(2)	1.439(5)	N(14)—H(14A)	0.8900
Co(1)—N(12)	1.955(3)	N(5)—C(1)	1.446(5)	N(11)—H(11A)	0.8900	N(14)—H(14B)	0.8900
Co(1)—N(13)	1.957(3)	N(6)—C(2)	1.318(4)	N(11)—H(11B)	0.8900	N(14)—H(14C)	0.8900
N(1)—C(1)	1.312(4)	N(6)—N(7)	1.328(4)	N(11)—H(11C)	0.8900	Cl(1)—O(8)	1.274(5)
N(1)—N(2)	1.329(4)	N(7)—N(8)	1.329(4)	N(12)—H(12A)	0.8900	Cl(1)—O(6)	1.389(6)
N(2)—N(3)	1.321(4)	N(8)—N(9)	1.325(5)	N(12)—H(12B)	0.8900	Cl(1)—O(7)	1.422(4)
N(3)—N(4)	1.330(5)	N(9)—C(2)	1.314(5)	N(12)—H(12C)	0.8900	Cl(1)—O(5)	1.429(4)

bond	bond angles / (°)	bond	bond angles / (°)	bond	bond angles / (°)	bond	bond angles / (°)
N(2)—Co(1)—N(7)	90.06(12)	N(2)—N(3)—N(4)	107.8(3)	Co(1)—N(11)—H(11B)	109.5	H(14A)—N(14)—H(14B)	109.5
N(2)—Co(1)—N(11)	89.77(11)	C(1)—N(4)—N(3)	103.6(3)	H(11A)—N(11)—H(11B)	109.5	Co(1)—N(14)—H(14C)	109.5
N(7)—Co(1)—N(11)	90.19(11)	C(1)—N(4)—H(4)	128.2	Co(1)—N(11)—H(11C)	109.5	H(14A)—N(14)—H(14C)	109.5
N(2)—Co(1)—N(14)	88.69(13)	N(3)—N(4)—H(4)	128.2	H(11A)—N(11)—H(11C)	109.5	H(14B)—N(14)—H(14C)	109.5
N(7)—Co(1)—N(14)	178.44(12)	O(1)—N(5)—O(2)	125.0(3)	H(11B)—N(11)—H(11C)	109.5	N(1)—C(1)—N(4)	115.5(3)
N(11)—Co(1)—N(14)	90.74(12)	O(1)—N(5)—C(1)	117.8(3)	Co(1)—N(12)—H(12A)	109.5	N(1)—C(1)—N(5)	121.9(3)
N(2)—Co(1)—N(12)	178.16(13)	O(2)—N(5)—C(1)	117.2(3)	Co(1)—N(12)—H(12B)	109.5	N(4)—C(1)—N(5)	122.6(3)
N(7)—Co(1)—N(12)	89.12(13)	C(2)—N(6)—N(7)	102.1(3)	H(12A)—N(12)—H(12B)	109.5	N(9)—C(2)—N(6)	114.3(3)
N(11)—Co(1)—N(12)	88.58(13)	N(6)—N(7)—N(8)	111.3(3)	Co(1)—N(12)—H(12C)	109.5	N(9)—C(2)—N(10)	123.6(3)
N(14)—Co(1)—N(12)	92.16(14)	N(6)—N(7)—Co(1)	125.6(2)	H(12A)—N(12)—H(12C)	109.5	N(6)—C(2)—N(10)	122.1(3)
N(2)—Co(1)—N(13)	90.52(14)	N(8)—N(7)—Co(1)	123.1(2)	H(12B)—N(12)—H(12C)	109.5	O(8)—Cl(1)—O(6)	110.7(8)
N(7)—Co(1)—N(13)	89.70(13)	N(9)—N(8)—N(7)	107.5(3)	Co(1)—N(13)—H(13A)	109.5	O(8)—Cl(1)—O(7)	114.4(4)
N(11)—Co(1)—N(13)	179.68(14)	C(2)—N(9)—N(8)	104.7(3)	Co(1)—N(13)—H(13B)	109.5	O(6)—Cl(1)—O(7)	103.9(4)
N(14)—Co(1)—N(13)	89.38(14)	C(2)—N(9)—H(9)	127.7	H(13A)—N(13)—H(13B)	109.5	O(8)—Cl(1)—O(5)	115.4(5)
N(12)—Co(1)—N(13)	91.12(15)	N(8)—N(9)—H(9)	127.7	Co(1)—N(13)—H(13C)	109.5	O(6)—Cl(1)—O(5)	99.6(5)
C(1)—N(1)—N(2)	101.4(3)	O(3)—N(10)—O(4)	125.2(3)	H(13A)—N(13)—H(13C)	109.5	O(7)—Cl(1)—O(5)	111.2(3)
N(3)—N(2)—N(1)	111.7(3)	O(3)—N(10)—C(2)	118.1(3)	H(13B)—N(13)—H(13C)	109.5		
N(3)—N(2)—Co(1)	123.8(2)	O(4)—N(10)—C(2)	116.7(3)	Co(1)—N(14)—H(14A)	109.5		
N(1)—N(2)—Co(1)	124.5(2)	Co(1)—N(11)—H(11A)	109.5	Co(1)—N(14)—H(14B)	109.5		

表4 BNCP分子中键的扭转角

Table 4 Torsion angles for BNCP

bond	angle/(°)	bond	angle/(°)	bond	angle/(°)	bond	angle/(°)
C(1)—N(1)—N(2)—N(3)	-0.4(3)	N(1)—N(2)—N(3)—N(4)	0.8(4)	N(14)—Co(1)—N(7)—N(8)	-68(5)	O(1)—N(5)—C(1)—N(4)	-8.4(5)
C(1)—N(1)—N(2)—Co(1)	-180.0(2)	Co(1)—N(2)—N(3)—N(4)	-179.6(3)	N(12)—Co(1)—N(7)—N(8)	77.0(3)	O(2)—N(5)—C(1)—N(4)	172.1(4)
N(7)—Co(1)—N(2)—N(3)	120.4(3)	N(2)—N(3)—N(4)—C(1)	-0.8(4)	N(13)—Co(1)—N(7)—N(8)	-14.1(3)	N(8)—N(9)—C(2)—N(6)	-0.2(4)
N(11)—Co(1)—N(2)—N(3)	-149.4(3)	C(2)—N(6)—N(7)—N(8)	-0.4(4)	N(6)—N(7)—N(8)—N(9)	0.3(4)	N(8)—N(9)—C(2)—N(10)	-178.8(3)
N(14)—Co(1)—N(2)—N(3)	-58.6(3)	C(2)—N(6)—N(7)—Co(1)	-179.5(2)	Co(1)—N(7)—N(8)—N(9)	179.5(2)	N(7)—N(6)—C(2)—N(9)	0.4(4)
N(12)—Co(1)—N(2)—N(3)	-176(4)	N(2)—Co(1)—N(7)—N(6)	74.4(3)	N(7)—N(8)—N(9)—C(2)	-0.1(4)	N(7)—N(6)—C(2)—N(10)	179.0(3)
N(13)—Co(1)—N(2)—N(3)	30.7(3)	N(11)—Co(1)—N(7)—N(6)	-15.4(3)	N(2)—N(1)—C(1)—N(4)	-0.2(4)	O(3)—N(10)—C(2)—N(9)	-177.9(3)
N(7)—Co(1)—N(2)—N(1)	-60.0(3)	N(14)—Co(1)—N(7)—N(6)	111(4)	N(2)—N(1)—C(1)—N(5)	-178.2(3)	O(4)—N(10)—C(2)—N(9)	2.4(5)
N(11)—Co(1)—N(2)—N(1)	30.1(2)	N(12)—Co(1)—N(7)—N(6)	-104.0(3)	N(3)—N(4)—C(1)—N(1)	0.6(5)	O(3)—N(10)—C(2)—N(6)	3.7(5)
N(14)—Co(1)—N(2)—N(1)	120.9(3)	N(13)—Co(1)—N(7)—N(6)	164.9(3)	N(3)—N(4)—C(1)—N(5)	178.6(3)	O(4)—N(10)—C(2)—N(6)	-176.1(3)
N(12)—Co(1)—N(2)—N(1)	3(4)	N(2)—Co(1)—N(7)—N(8)	-104.6(3)	O(1)—N(5)—C(1)—N(1)	169.5(3)		
N(13)—Co(1)—N(2)—N(1)	-149.7(3)	N(11)—Co(1)—N(7)—N(8)	165.6(3)	O(2)—N(5)—C(1)—N(1)	-10.0(5)		

参考文献:

- [1] Bates L R. The potential for tetrazoles in initiating explosive systems [A]. Proceedings of the 13th Symposium on Explosives and Pyrotechnics[C], Hilton Head Island, S. C., P. III - 1, Dec. 2 - 4, 1986.
- [2] John Fronabarger, Alex Schuman, Robert D Chapman, et al. Chemistry and development of BNCP, a novel DDT explosive [A]. International Symposium Energetic Materials Technology[C], March 21 - 24, 1994, Florida, USA.
- [3] Fyfe D W, Fronabarger J W, Bickes Jr R W. BNCP prototype detonator studies using a semiconductor bridge initiator [A]. Proceedings Twentieth International Pyrotechnics Seminar[C], 25 - 29 July 1994, Colorado, U. S. A.
- [4] John W Fronabarger, Willian B Sanborn, Tom Massis. Recent activities in the development of the explosive - BNCP [A]. 22th International Pyrotechnics Seminar[C], Fort Colorado, 15 - 19 July 1996.
- [5] Marx K D, Ingersoll D, Bickes Jr R W. Electrical modeling of semiconductor bridge (SCB) BNCP detonators with electrochemical capacitor firing sets [A]. 24th International Pyrotechnics Seminar Monterey [C], California, 27 - 31 July, 1998.
- [6] Ewick David W, Bateas Gus, Riley Scot P, et al. Laser-ignitable Ignition composition and initiator devices and assemblies comprising the same [P]. WO99/00343, PCT/US98/12583.

- [7] 盛涤伦, 马凤娥, 孙飞龙, 等. BNCP 起爆药的合成及其主要性能[J]. 含能材料, 2000, 8(3): 100-103.
SHENG Di-lun, MA Feng-e, SUN Fei-long, et al. Study on synthesis and main properties of BNCP[J]. *Chinese Journal of Energetic Materials (Hanneng Cailiao)*, 2000, 8(3): 100-103.
- [8] Morosion B, Dunn R G, Assink R, et al. The secondary explosive tetraamine-cis-bis(5-nitro-2H-tetrazolato-N2) cobalt (III) perchlorate at 293 and 213 K[J]. *Acta Crystallographica Section C*, 1997, 53: 1609-1611.

Crystal Structure of Initiating Explosive BNCP

SHENG Di-lun, MA Feng-e, ZHANG Yu-feng, ZHU Ya-hong, CHEN Li-kui, YANG Bin

(Shaanxi Applied Physics and Chemistry Research Institute, Xi'an 710061, China)

Abstract: The single crystal of tetraaminebis(5-nitrotetrazolato) cobalt (III) perchlorate (BNCP) was prepared and characterized by elemental analysis and X-ray single crystal diffraction. The results prove that the crystal is monoclinic. Space group is $P2(1)/n$ with crystal parameters of the unit cell dimensions: $a = 10.0149(11) \text{ \AA}$, $\alpha = 90^\circ$, $b = 10.5387(11) \text{ \AA}$, $\beta = 109.0140(10)^\circ$, $c = 14.8241(16) \text{ \AA}$, $\gamma = 90^\circ$, $V = 1479.2(3) \text{ \AA}^3$, $Z = 4$, $D_c = 2.050 \text{ mg} \cdot \text{mm}^{-3}$, $\mu = 1.421 \text{ mm}^{-1}$, $F(000) = 928$. The information is also provided about atomic coordinates, equivalent isotropic displacement parameters, bond lengths, bond angles and torsion angles of BNCP. On the basis of tested parameters, the structure characteristics and decomposed mechanism of BNCP were obtained.

Key words: physical chemistry; initiating explosive; tetraaminebis(5-nitrotetrazolato) cobalt (III) perchlorate (BNCP); crystal structure; monoclinic system

(上接 491 页)

积极探索其它的既能简便易行地搭成笼子又能兼顾在硝解中易于离去,使二者能够统一起来,这才是实现两步法合成成功的巨大挑战。

参考文献:

- [1] 赵信岐, 方涛, 孙成辉. 六硝基六氮杂异伍兹烷制备工艺研究开发新进展[J]. 兵工学报, 2004, 25(3): 354-358.
ZHAO Xin-qi, FANG Tao, SUN Cheng-hui. Research and development of HNIW synthesis[J]. *Acta Armamentarii*, 2004, 25(3): 354-358.
- [2] Nielsen A T, Nissan R A, Vanderah D J. Polyazapolycyclics by condensation of aldehydes with amine. 2. Formation of 2, 4, 6, 8, 10, 12-hexabenzyl-2, 4, 6, 8, 10, 12-hexaazatetrayclo[5. 5. 0. 0^{5,9}. 0^{3,11}] dodacanes from glyoxal and benzylamines[J]. *J Org Chem*, 1990, 55: 1459-1466.
- [3] Surapaneni, Damavarapu. Energetic materials, analysis, diagnostics and testing, process improvements in CL-20 manufacture[A]. 31st Annual International Conference of the ICT[C], Jun. 27-30, 2000. Karlsruhe (Germany), 108-1-108-4.
- [4] Klapotke T M, Krumm B, Piotrowski H, et al. Synthesis and structures of trifluoromethyl-, fluoro-, and azido-substituted hexabenzylhexaazaisowurtzitane and isolation of a novel hexaazaisowurtzitane-based polycycle[J]. *Chem Eur J*, 2003, 9: 687-694.
- [5] Guy Cagnon, Genevieve Eck, Gregoire Herve, et al. Process for the 2-stage synthesis of hexanitrohexaazaisowurtzitane starting from a primary amine[P]. US20040260086A1. 2004. 12. 23.
- [6] Gregoire Herve, Guy Jacob, Roger Gallo. Preparation and structure of novel hexaazaisowurtzitane cages[J]. *Chem Eur J*, 2006, 12: 3339-3344.

Synthesis of Hexaallylhexaazaisowurtzitane

LI Xin-le¹, SUN Cheng-hui¹, ZHAO Xin-qi¹, SONG Jian-wei²

(1. School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China;

2. Liaoning Qingyang Chemical Industry Corporation, Liaoyang 111000, China)

Abstract: In order to explore a new route for the synthesis of CL-20, hexaallylhexaazaisowurtzitane was synthesized by condensation reaction of allylamine with aqueous glyoxal without inert gases protection. Its structure was characterized by FTIR, ¹H NMR and ¹³C NMR. This route has higher yield of 37.1% and easier way than the literature. Hexaallylhexaazaisowurtzitane without benzyl group in the molecule would be a potential nitrolyzable precursor to CL-20.

Key words: organic chemistry; hexaallylhexaazaisowurtzitane; synthesis; CL-20